CHEMICAL SURFACE TREATMENT OF TITANIUM

to

WATERTOWN ARSENAL

October 30, 1953

FINAL REPORT

on

CHEMICAL SURFACE TREATMENT OF TITANIUM

to

WATERTOWN ARSENAL

October 30, 1953

by

H. A. Pray, P. D. Miller, and Richard A. Jefferys

Contract No. DA-33-019-ORD-215
W.A.L. File No. 401/45-33
O.O. Project No. TB4-15
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FINAL REPORT

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Ordnance District: Cleveland

Contract Number: DA-33-019-ORD-215, W.A.L. File No. 401/45-33

O.O. Project Number: TB4-15

D/A Project Number: 593-08-021

Title: Chemical Surface Treatment of Titanium

Authors: H. A. Pray, P. D. Miller, and Richard A. Jefferys

Object: To initiate development and operation of various chemical and electrochemical surface treatments of titanium and its alloys, with emphasis upon practical application.

Summary: This is the final report under Contract No. DA-33-019-ORD-215 on the "Chemical Surface Treatment of Titanium". It contains a discussion of the research conducted during the contract period from May 23, 1951, to October 30, 1953.

The investigation of surface treatments for titanium has resulted in the development of two types of baths that produce adherent, continuous coatings on titanium and its alloys. The first type is represented by a 5 per cent sodium hydroxide anodic bath and the second by the fluoride-phosphate and the fluoride-borate immersion baths.

Considerable attention has been given to the evaluation of these coatings. As a consequence, it has been shown that they are quite useful in several fields.

For example, the coatings minimize greatly the severe galling tendency of titanium. Extensive laboratory tests have shown that they are useful in wire or tube drawing. By comparison with present commercial methods for drawing titanium, such coatings show important possibilities in the future fabrication and use of the metal.

It was found that certain treatments produced coatings that provided good service for various types of reciprocating and rotary wear. Samples ran continuously for over a month in reciprocating wear at 2500 psi and for several hundred hours in more severe rotary wear. These treatments involved coating the titanium in an immersion bath to produce an adherent,

continuous crystalline coating, followed by (1) a heat treatment in air at about 800 F for 3 hours or by (2) application of a MoS_2-Epon resin mixture.

It is felt that these processes are of considerable potential usefulness because wear resistance can be produced at temperatures below those at which any phase transformation of the metal can occur. The wear resistance is comparable to that for carbonized or nitrided surfaces which require high-temperature treatments, resulting in damage to the core properties.

Paint-adhesion tests have shown value for the surface conversion coatings in paint applications on titanium articles.

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INTRODUCTION

The development of surface coatings and conversion films has increased the usefulness of many metals. For example, aluminum, magnesium, and steel have found extended application because of useful surface properties produced by chemical treatments. Wear resistance, ease of forming and drawing, corrosion resistance, paint adhesion, and decorative effects have been improved. While the corrosion resistance of titanium exceeds that of most metals, its use is limited by the tendency to gall and seize when placed in loaded contact with another metal.

The research program established under the subject contract included: (1) a basic study of chemical and electrochemical reactions of titanium, and (2) the development of practical treatments to minimize or alleviate the problems encountered in titanium applications. Such applications might be wear, cold drawing and forming, resistance to oxidation, and paint adhesion.

EXPERIMENTAL WORK

Anodic-Coating Development

An extensive investigation of anodic treatments on titanium was made. In general, titanium reacts anodically to form thin, colored films of little value. However, a few aqueous baths were found which would produce fairly thick anodic coatings. Table 1 shows the compositions and operating conditions of the most promising anodic baths.

Of the many anodic baths studied, the 5 per cent NaOH bath gave the best coating. The coating was sparkling gray and adherent, and possessed a smooth slippery surface. Evaluation tests of this coating are discussed later.

The pretreatment given to all specimens before anodizing was a hot sodium metasilicate degrease followed by a water rinse and an acid pickle in a solution of:

900 ml/l 1-1 HNO_3 + H_2O
100 g/l $NH_4F \cdot HF$
100 ml/l H_2SiF_6

This solution removed any scale or oxide film that might be present.

The composition and the nature of the titanium surface were found to influence the formation of the anodic coating. When a sample was alloyed, the current density and time had to be increased as the amounts of alloying additions increased. Also, the effects of work hardening or surface grinding necessitated a change in coating conditions to obtain a satisfactory coating.

Chemical-Coating Development

From a commercial standpoint, the advantages of coating by chemical reaction are obvious. A detailed study was made to find baths which would coat titanium by simple immersion. The most promising of the baths developed are shown in Table 2. Of these, there are two compositions that furnish useful immersion coatings on titanium. They are (1) a fluoride-phosphate bath and (2) a fluoride-borate bath.

TABLE 1. ANODIC-COATING BATHS

Bath No.	Bath Composition	Temperature, C	Time, minutes	Current Density, amp/ft^2	Description of Coating
194	100g NaOH 1900g H_2O	95	20	50	Sparkling gray; durable coat
76	25g $NaAlO_2$ 5g $NaH_2PO_4 \cdot H_2O$ 475g H_2O	90	20	25-50	Gray green; fairly hard coat
91	25 g Na_2O_2 5g $NaH_2PO_4 \cdot H_2O$ 500g H_2O	45	25	50	White; fairly hard coat
155	375g $NaClO_3$ 375g H_2O	25	30	7-12	Salty-white coat
168	800g $Na_2CO_3 \cdot 10H_2O$ 800g H_2O	95	10	25	Thin gray; fairly adherent coat
164	100g $NaClO_3$ 900g H_2O	25	20	3	Thin, very hard green coat
148	10g NH_4HF_2 25g NH_4OH 450g H_2O 10g $NH_4H_2PO_4$	80	10	35	Blue-white coat

TABLE 2. CHEMICAL-COATING BATHS

Bath No.	Bath Composition	Temperature, C	Coating Time, minutes	pH	Description of Coating
1	50g/l $Na_3PO_4 \cdot 12H_2O$ 20g/l $KF \cdot 2H_2O$ 11.5ml/l HF solution(1)	85	10	5.1-5.2	Light silver gray; durable coating
2	50g/l $Na_3PO_4 \cdot 12H_2O$ 50g/l $KF \cdot 2H_2O$ 26ml/l HF solution(1)	25	1-2	>1.0	Dark, metallic gray; adherent coating
3	40g/l $Na_2B_4O_7 \cdot 10H_2O$ 18g/l $KF \cdot 2H_2O$ 16g/l HF solution(1)	85	20	6.3-6.6	Metallic gray; adherent coat
4	30g/l $Na_2C_2O_4$ 20g/l $KF \cdot 2H_2O$ 1ml/l HF solution(1)	60	30	4.1	Dark-gray coating (not reproducible)
5	75g/l $K_2C_2O_4 \cdot H_2O$ 25g/l $KF \cdot 2H_2O$ 3ml/l HF solution(1)	65	30	4.6	Light-gray coating (not reproducible)

(1) 50.3 per cent HF by weight.

The immersion-coating procedure consisted of:

(1) Hot alkaline degrease (sodium metasilicate)
(2) Cold H_2O rinse
(3) $HF-HNO_3$ pickle (as described previously under anodizing)
(4) Cold H_2O rinse
(5) Immersion in a chemically active bath
(6) Cold H_2O rinse and dry

The coating obtained from the high-temperature, fluoride-phosphate bath (No. 1, Table 2) on Ti-75, RC-55, and Ti-130B was light silver gray in appearance and possessed good adhesion to the base metal. No satisfactory coating was obtained on Ti-130A or 150A. The coatings have a composition of approximately 39 per cent fluoride, 3 per cent phosphate, 25 per cent potassium, and 17 per cent titanium, indicating the formation of a potassium-titanium fluoride complex.

The two most important variables of bath operation were temperature and pH. Several common methods of pH control were tried and were found to be unsatisfactory for use in a bath containing dissolved titanium and the active fluoride ion. A spectrophotometric method proved to be the best way to maintain accurate pH control of this bath. The thickness of the coating and the degree of adhesion to the base metal depended on the immersion time (Figure 1).

At a higher acid content (No. 2, Table 2), the fluoride-phosphate bath operated at room temperature and coated all five commercial alloys. The operating procedure was the same as outlined previously. The coating was metallic gray and adherent to the base metal, and formed a hard, glazed surface when rubbed under pressure.

The immersion time and the free-acid content must be controlled to obtain satisfactory coatings. Figure 2 shows the relationship of immersion time to the amount of coating formed.

The degree of acidity was followed by a titrimetric analysis. A 20-ml bath sample in 100 ml of distilled water was titrated with 1.0 N NaOH using a phenolphthalein indicator. The sample neutralized 11.5-12.0 ml 1.0 N NaOH, if the bath was in the proper coating range.

The second composition which formed coatings on titanium was a fluoride-borate bath. The coating obtained had a gray metallic luster and possessed good adhesion to the base metal. The bath coated all five commercial alloys. Figure 3 shows the relationship of the immersion time to the amount of coating formed.

As can be seen from Table 2, the room-temperature fluoride-phosphate bath is operative under conditions more suited to a commercial process than the others. It operated at room temperature and coated the five alloys

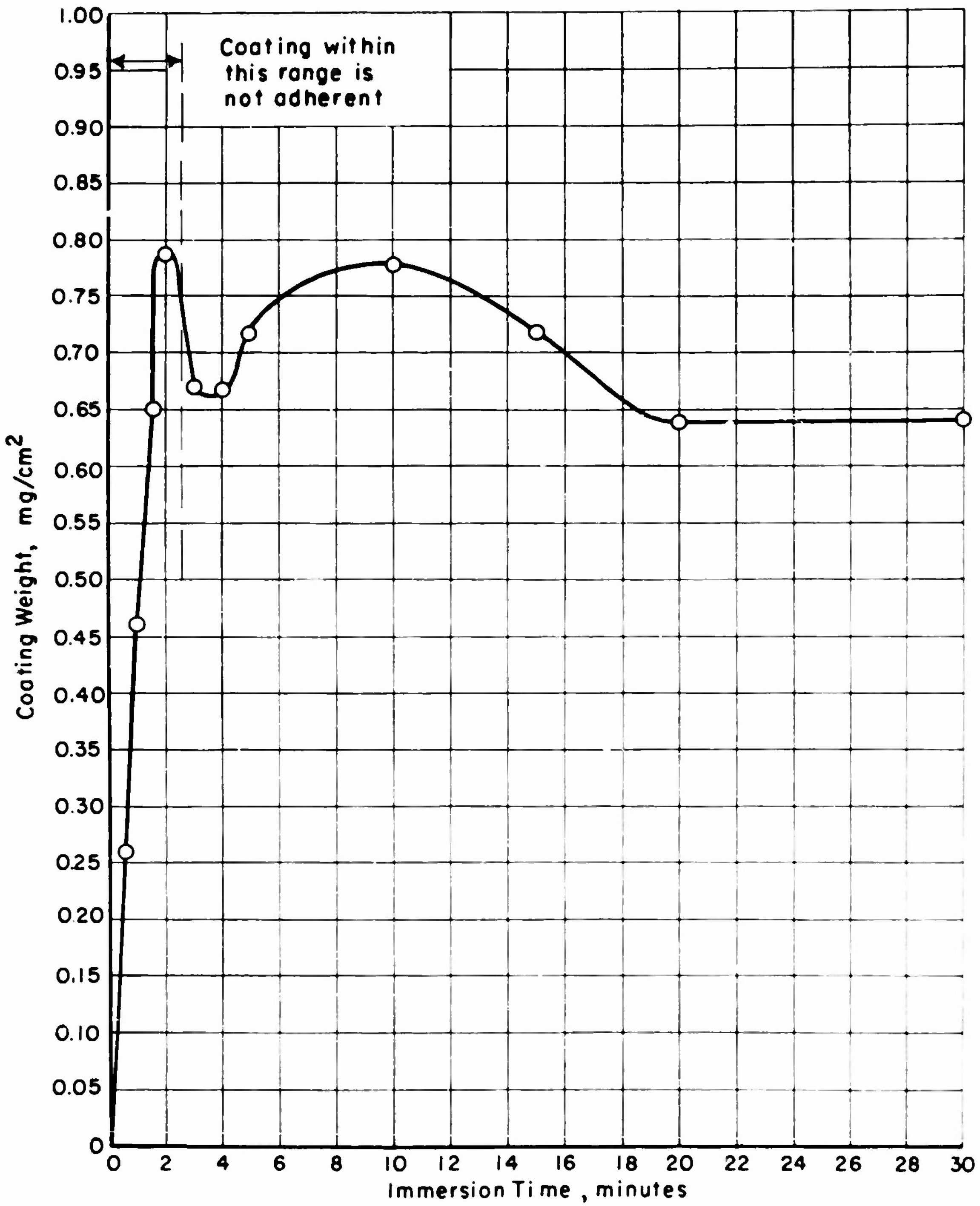

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FIGURE 1. COATING RATE OF HIGH-TEMPERATURE FLUORIDE-PHOSPHATE BATH

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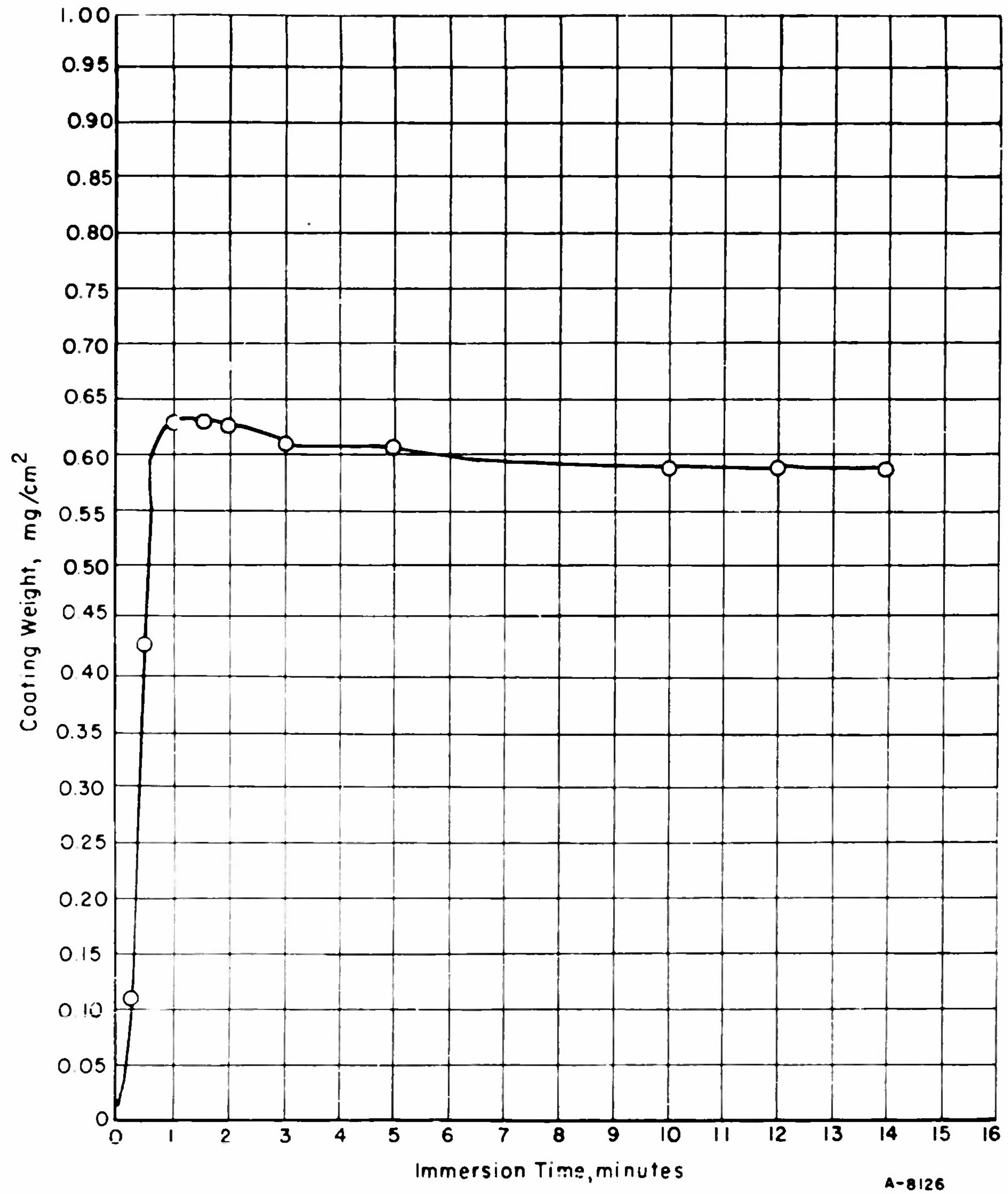

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FIGURE 2. COATING RATE OF ROOM-TEMPERATURE FLUORIDE-PHOSPHATE BATH

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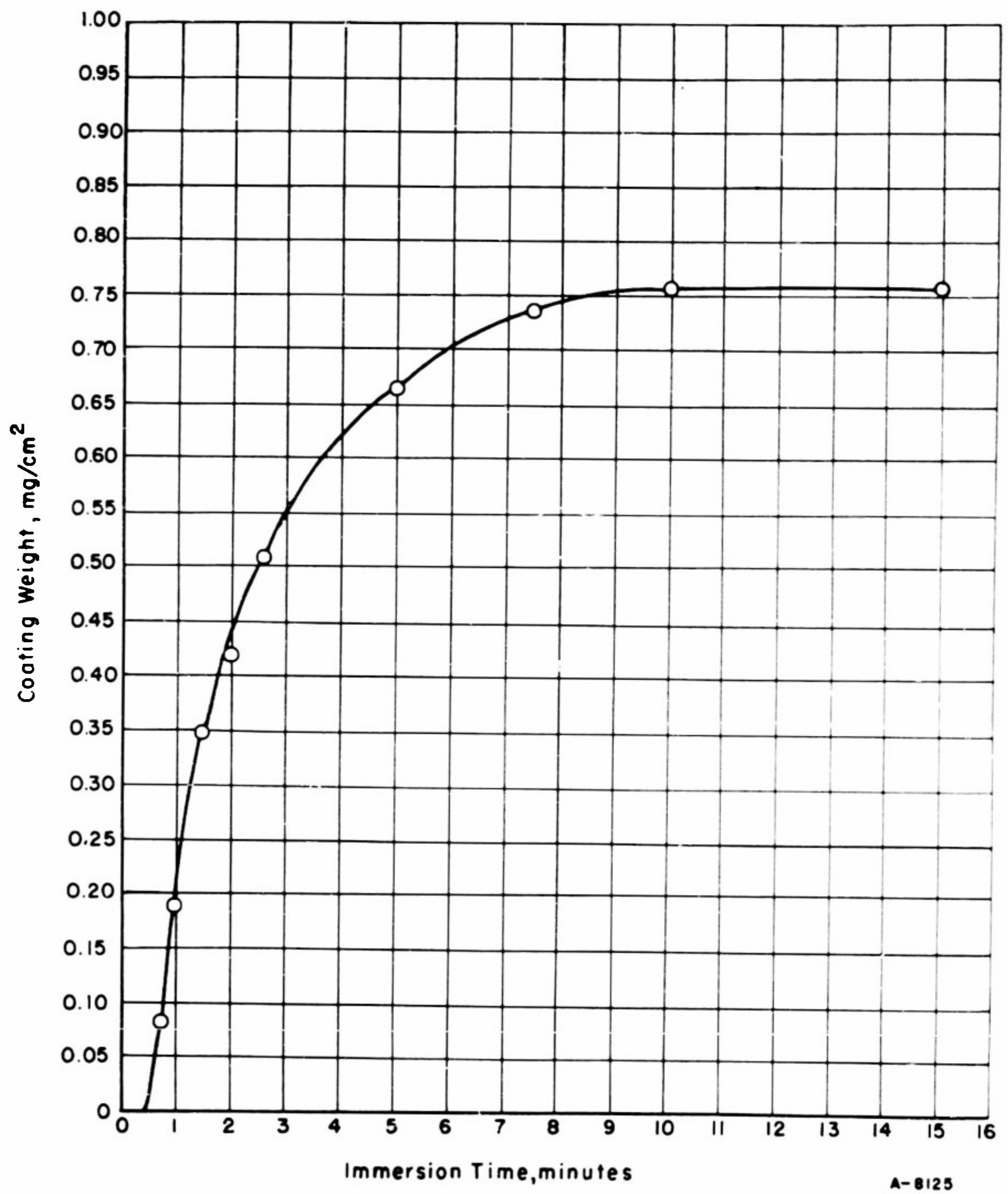

FIGURE 3. COATING RATE OF FLUORIDE-BORATE BATH

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studied in 1 to 2 minutes. It was also quite stable and required only a simple titration to maintain coating control.

The properties of the coatings are:

Variable	Coating Property
Color	Light silver gray to metallic gray
Solubility	Soluble in cold HCl, HNO_3, HF, and concentrated NaOH
	Soluble in boiling H_2O; turbid, milky solution formed
	Slightly soluble in cold H_2O
Adhesion	Good
Water of hydration	Removed at 212 F
Decomposition point	About 1200 F
Absorption	High for nonviscous fluids (water, ink, dyes, oils, etc.)
Electrical effects	Some indication of rectification
Chemical effects	Activation of surfaces giving increased oxidation rate

Treatment of Coatings

Heat Treatment

Remarkable wear properties resulted from the heating of immersion-coated titanium in air at 800 to 1000 F for 3 to 5 hours. The increase in wear was brought about by the formation of a layer of TiO_2 (anatase) at the crystalline coating - base metal interface. The coating apparently increases the oxidation rate of the titanium metal over that of untreated metal. Figures 4, 5, and 6 show this increase for fluoride-phosphate and fluoride-borate coated Ti-75A as compared with bare, untreated titanium.

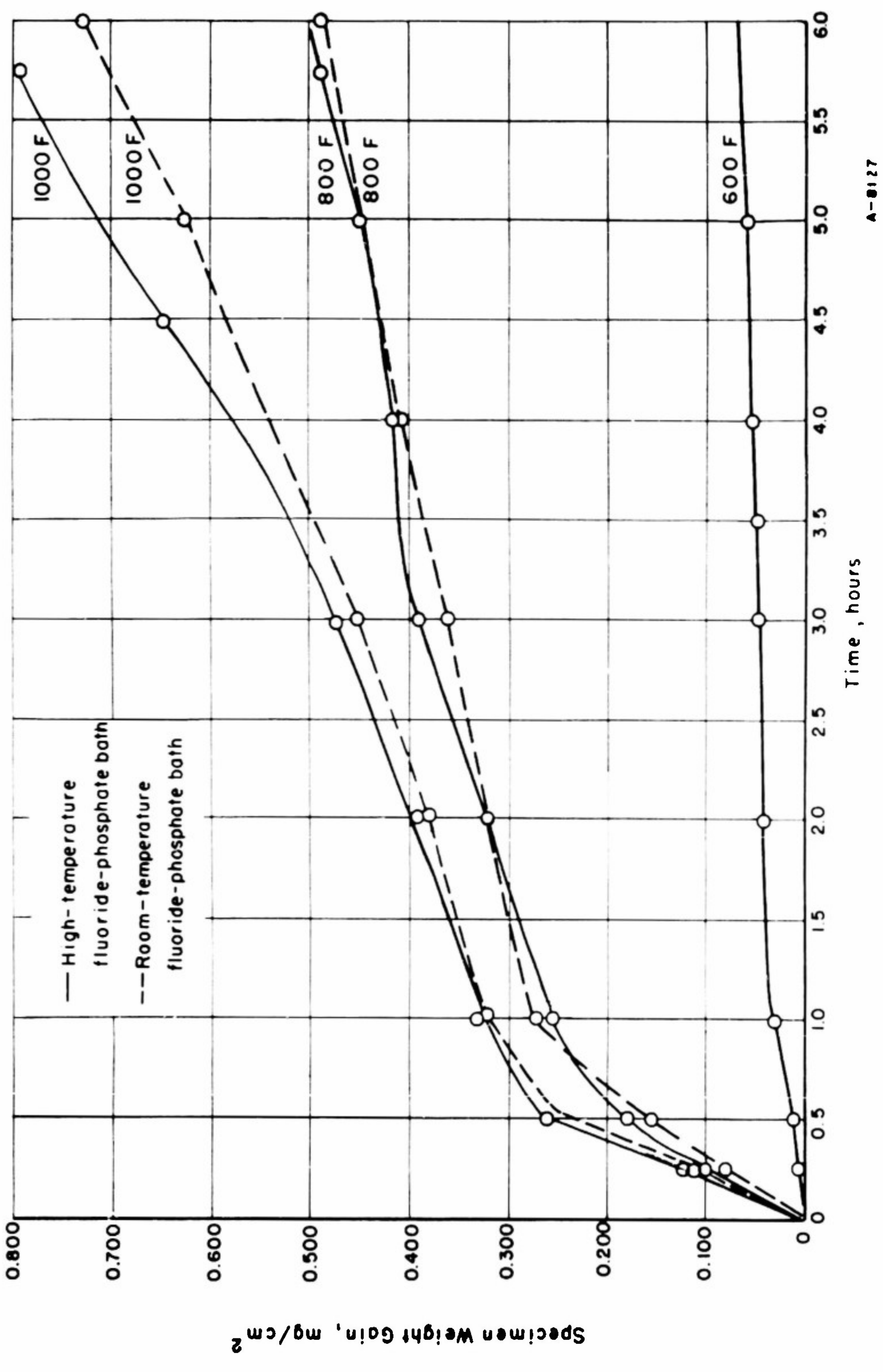

FIGURE 4. OXIDATION OF FLUORIDE-PHOSPHATE-COATED Ti-75 A AT VARIOUS TEMPERATURES

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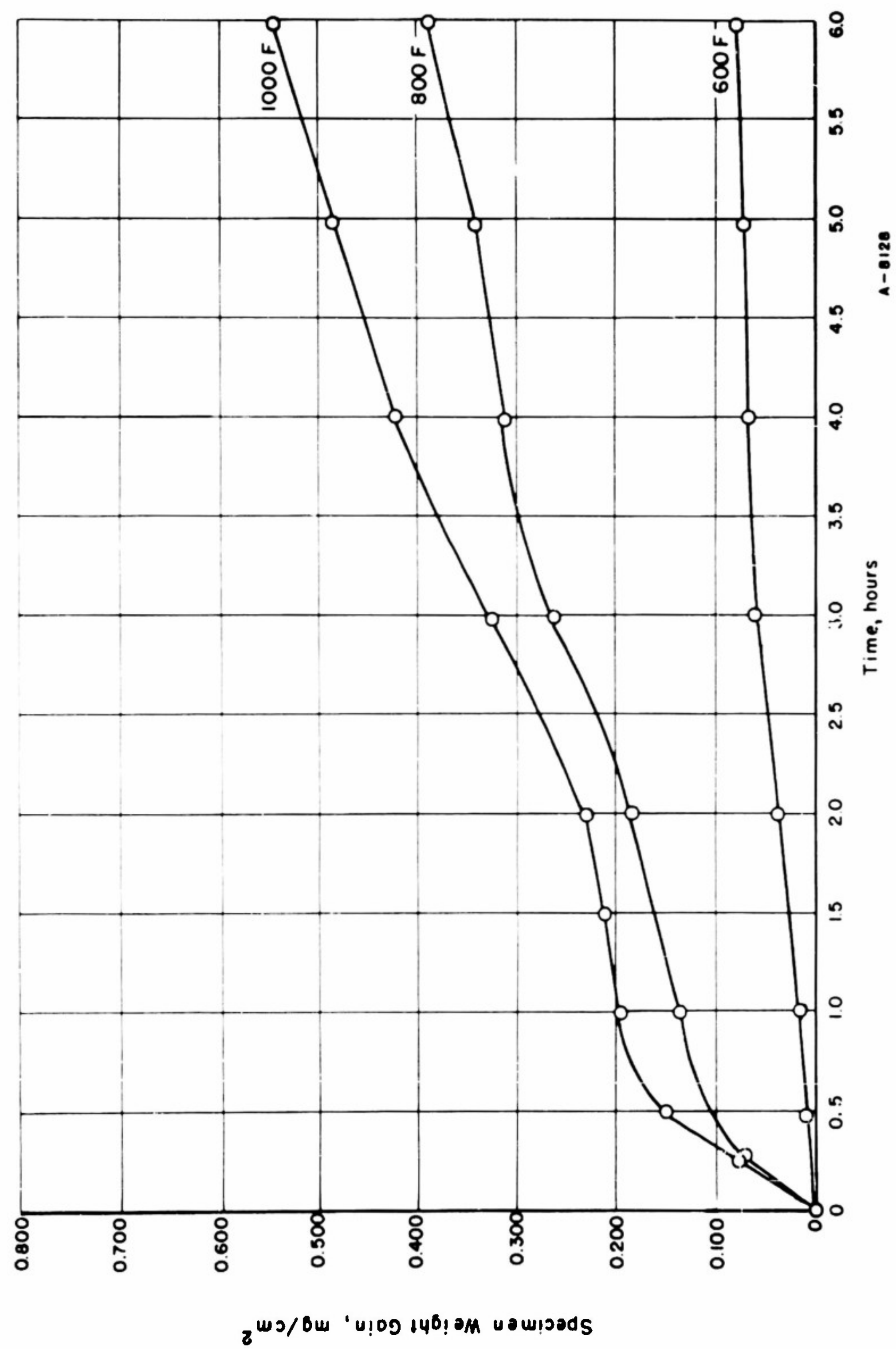

FIGURE 5. OXIDATION OF FLUORIDE-BORATE-COATED Ti-75 A AT VARIOUS TEMPERATURES

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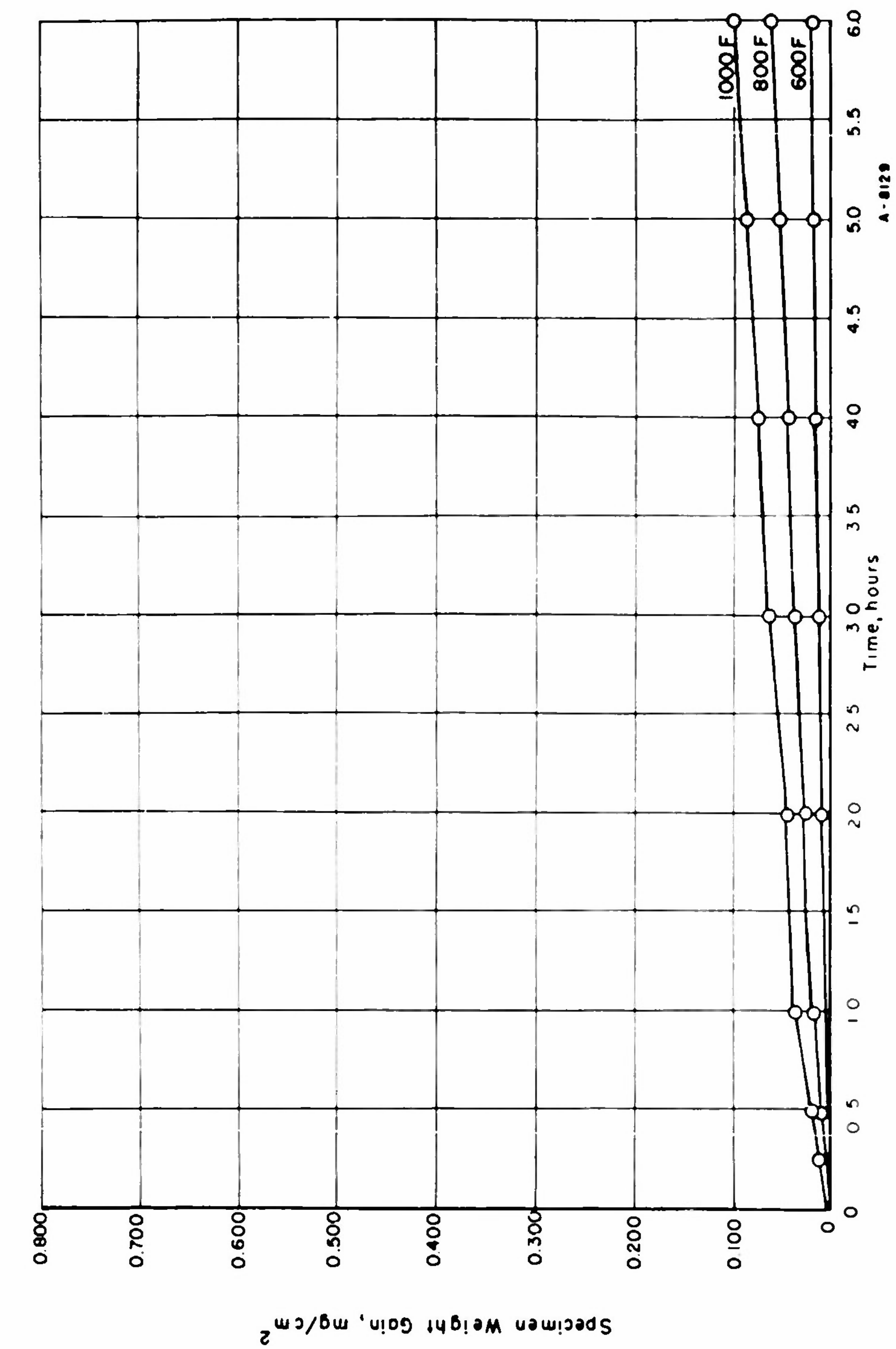

FIGURE 6. OXIDATION OF BARE Ti-75 A AT VARIOUS TEMPERATURES

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Lubrication

The wear of titanium metal was greatly improved by a thin layer of MoS_2 in an Epon phenolic resin (Synthetasine 100) bonded to the coated or the heat-treated, coated titanium metal. The MoS_2-Epon phenolic resin mixture (1:2 ratio), with just sufficient thinner to form a thick paste, is applied to the treated titanium surface, air dried 6 to 12 hours, cured for 12 hours at 300 F, and then burnished to the desired thickness. This treatment produced a hard, ebony-black surface capable of maintaining a continuous lubricating phase between a titanium and an opposing metal surface. The wear-test results of this combination, which are quite promising, are discussed later.

Evaluation and Application

Various types of tests were used to evaluate the coatings on titanium. These were: (1) seizure tests under extremely high contact pressures and involving severe deformation of the titanium metal, (2) wear tests involving relatively high loads and varying speeds, and (3) paint adhesion.

High-Pressure Wear

An ordinary shaper machine (Figure 7) was used to test the coatings at loads up to 70 tons per square inch. A steel ball (Figure 8) was drawn back and forth over the coated panel forming a grooved wear line. Table 3 shows the results of these tests for both anodic and immersion coatings. The tests were made under No. 30 machine oil at a machine speed of 25 strokes per minute with a 2-3/8-inch stroke. The fluoride-phosphate and fluoride-oxalate immersion coatings wore slightly longer than the anodic NaOH coatings. Bare titanium galled immediately and poor coatings failed rapidly.

Wire-Drawing Tests

The effectiveness of the immersion and the anodic coatings has been shown by the cold drawing of titanium wire and tubing, which is a severe test for surface coatings. Wire of Ti-75A, 100A, 150A, 175A, RC-130A, and 130B composition has been successfully drawn with an immersion or anodic coating and an additional lubricant (Table 4). Companion lubricants that have been tried successfully in drawing are: Molykote G, Houghton 3105, Dri Draw, MoS_2 in Duco Lacquer, Bonderlube 235, and sodium silicate-oleic acid. It is, however, necessary to have both the coating and the lubricant present. Figure 9 shows apparatus used in making drawing-force measurements. Figure 10 shows a comparison of the required drawing force of air-oxidized and immersion-coated titanium wire.

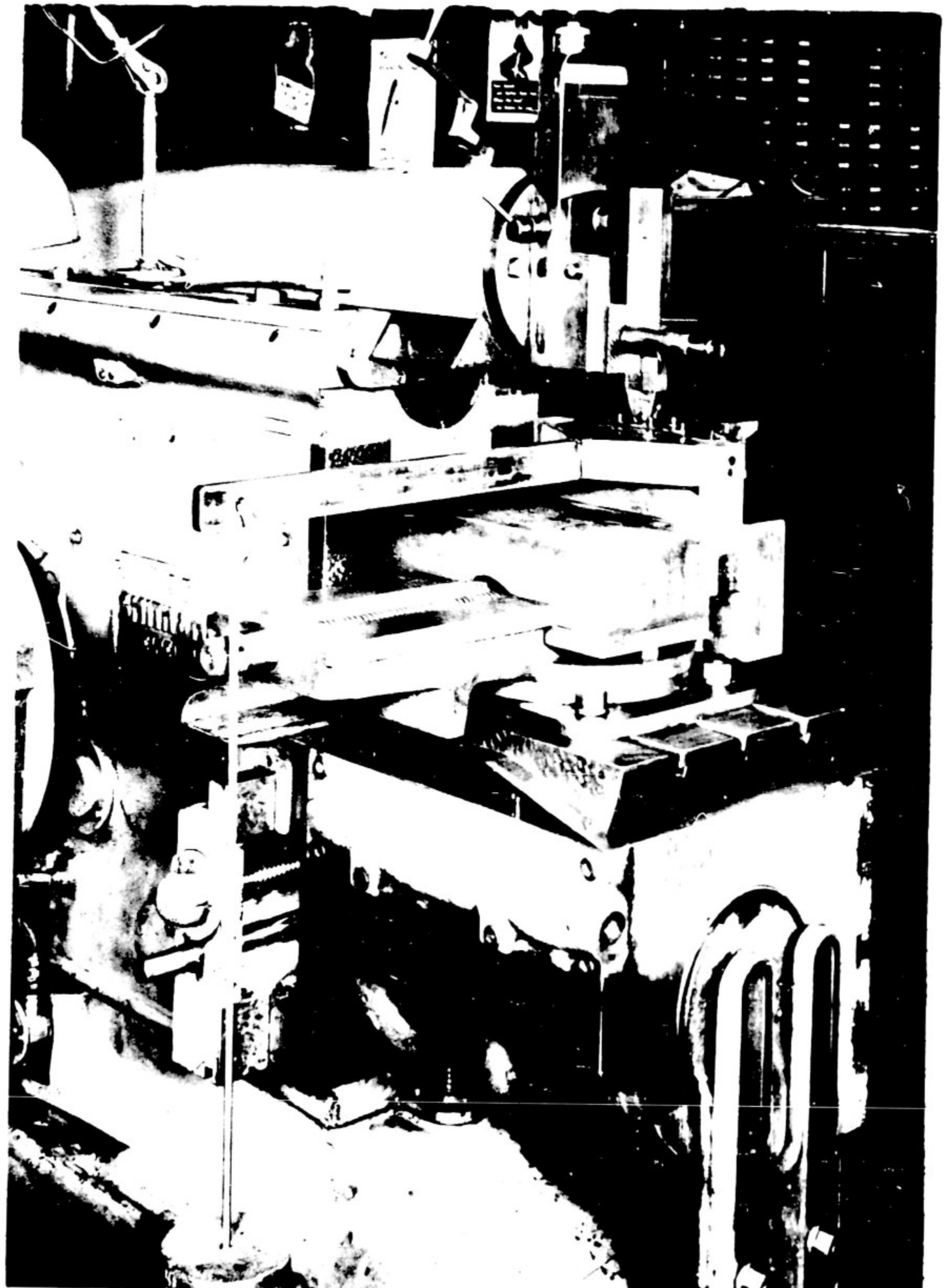

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FIGURE 7. ASSEMBLY USED FOR MEASURING SEIZURE ON ANODIZED TITANIUM

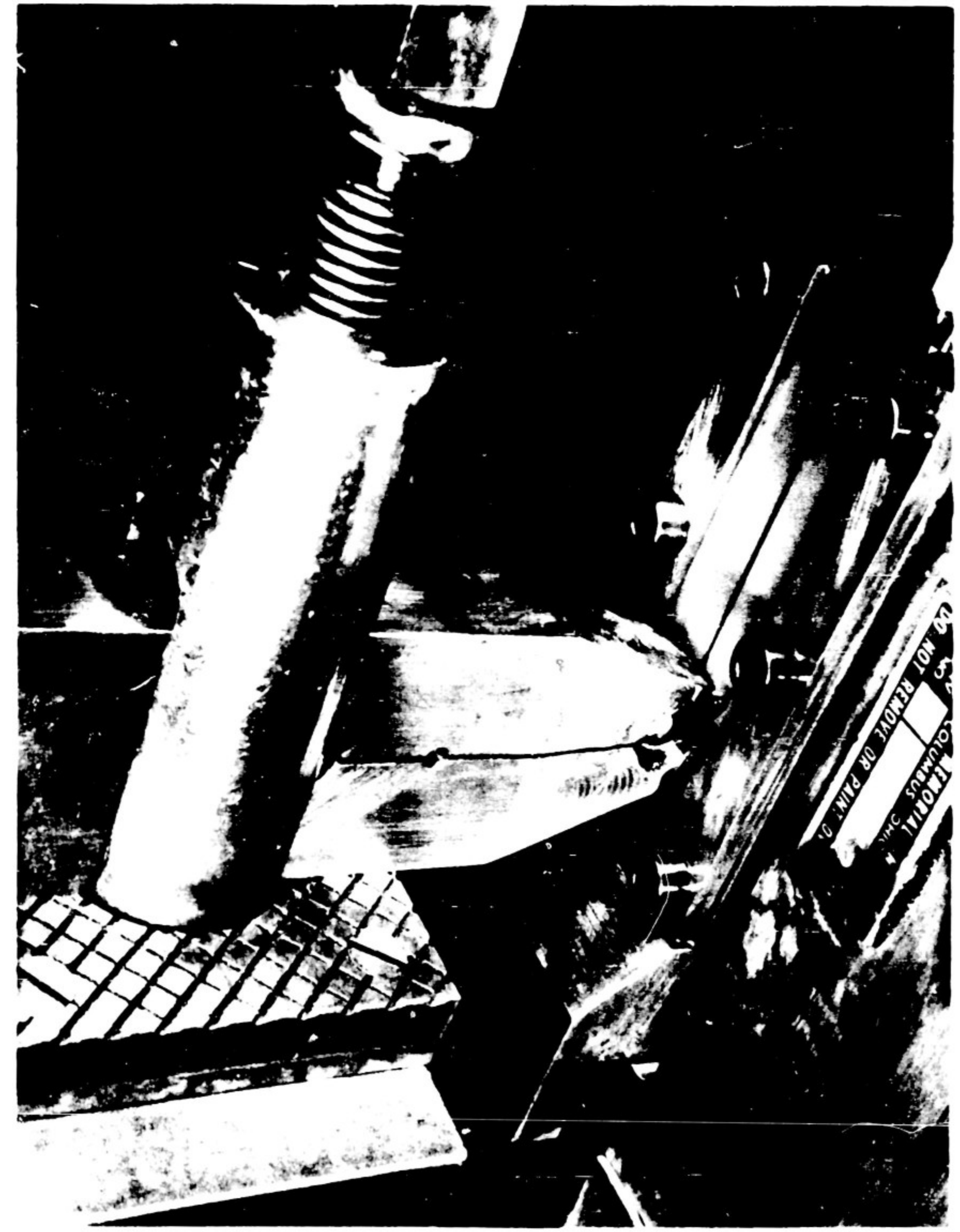

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FIGURE 8. SEIZURE-TEST APPARATUS USING BALL

TABLE 3. HIGH-PRESSURE SEIZURE TESTS OF COATED TITANIUM

Conditions: 2-3/8-Inch Stroke
25 Strokes per Minute
70 Tons per Square Inch
Contact Pressure

Specimen No.	Alloy	Type Coating	Lubricant	Number of Strokes	Remarks
1	RC-55	Bare	Molykote G	1	Galled
2	RC-55	Anodic 0.25% HBF_4	Molykote G	16	Galled
3	RC-130B	Anodic 5% NaOH, 2.5% Na_2CO_3	Machine oil	250	Rough wear track
4	RC-55	Anodic 5% NaOH	Molykote G	250	Smooth wear track
5	RC-55	Anodic 10% NaOH	Machine oil	250	Smooth wear track
6	RC-55	Fluoride-oxalate	Machine oil	250	Worn thin
7	RC-55	Fluoride-oxalate	Machine oil	500	Smooth wear track
8	RC-55	Fluoride-phosphate	Machine oil	250	Smooth wear track
9	RC-55	Fluoride-phosphate	Machine oil	375	Worn thin
10	RC-130B	Fluoride-phosphate	Machine oil	500	Smooth wear track
11	RC-55	Fluoride-phosphate	Molykote G	500	Smooth wear track
12	RC-55	Fluoride-phosphate	Molykote G	500	Smooth wear track, highly polished

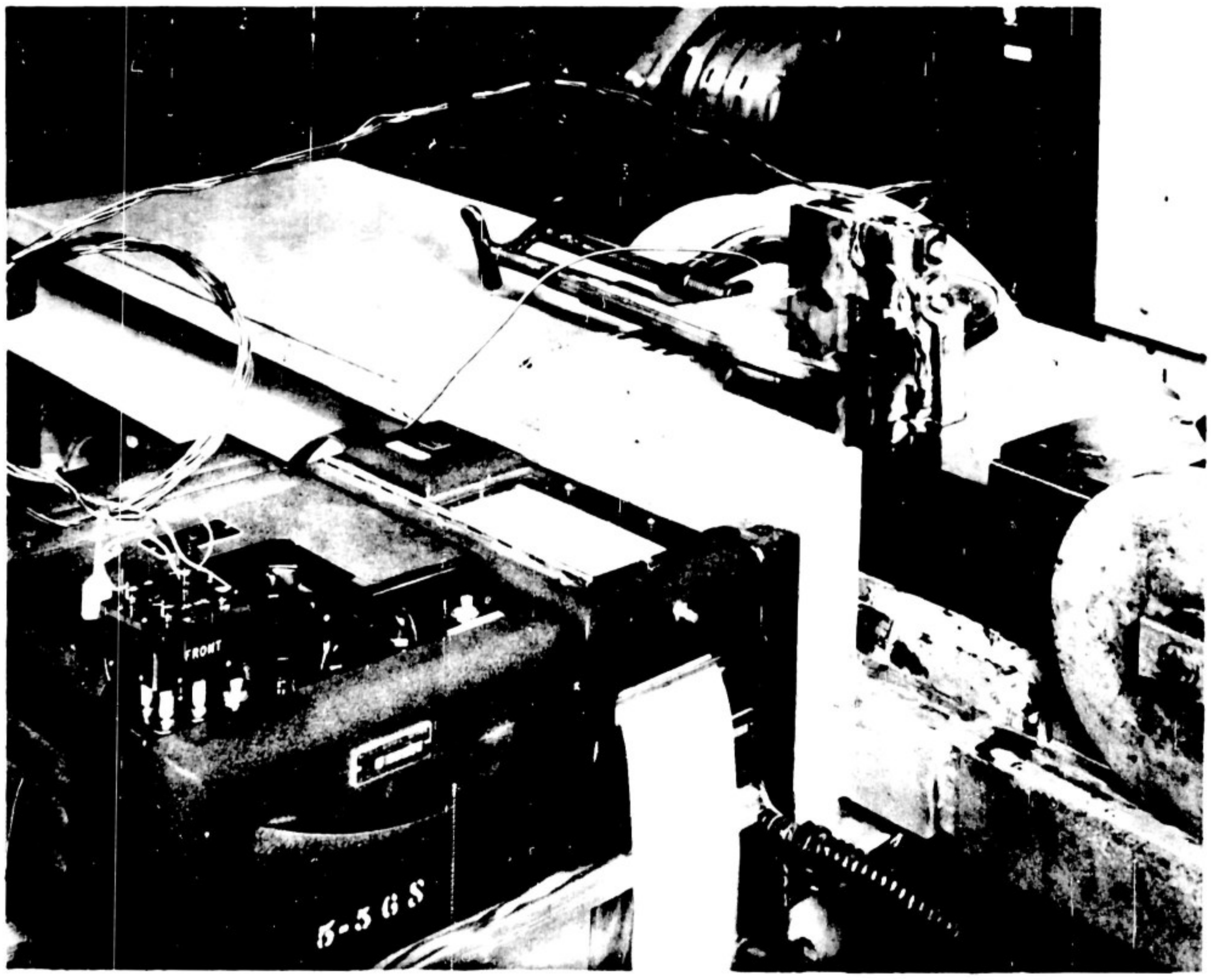

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FIGURE 9. APPARATUS FOR MEASURING DRAWING FORCE

TABLE 4. COLD DRAWING OF TITANIUM USING SURFACE COATINGS[1]

Example No.	Alloy	Treatment of Wire	Drawing Lubricant	Initial Diameter, inch	Final Diameter, inch	Per Cent Total Reduction	Total Number of Passes	Number of Times Coated	Final Condition of Wire
1	Ti-75A	Bare	Molykote G	0.125	--	--	0	1	Galled
2	Battelle 175A	Bare	Ditto	0.125	--	--	0	1	"
3	Ti-75A	10% NaOH anodic coating	"	0.125	0.110	22.5	2	1	Smooth, ungalled
4	Ti-100A	Ditto	"	0.110	0.059	71.2	7	1	Ungalled, score marks
5	Ti-100A	"	"	0.110	0.067	63.0	6	1	Galled and fractured
6	Ti-150A	"	"	0.110	0.094	27.0	3	1	Smooth, ungalled
7	RC-130A	5% NaOH anodic coating	"	0.125	0.110	22.5	2	1	Ditto
8	RC-130B	Ditto	Houghton 3105	0.125	0.110	22.5	3	1	Scored
9	RC-130B	"	Molykote G	0.125	0.110	22.5	2	1	"
10	Ti-75A	Fluoride-oxalate coating (185 F)	Ditto	0.061	0.051	30.0	4	1	Smooth
11	Ti-75A	Room-temperature fluoride-oxalate coating	"	0.061	0.054	21.5	3	1	Galled and fractured
12	Ti-75A	Fluoride-phosphate(A)[2] coating (185 F)	"	0.058	0.051	22.5	3	1	Scored
13	3% Cr, 1.5% Fe, 0.1% N	Ditto	"	0.242	0.204	29.0	3	1	"
14	Ti-75A	Fluoride-phosphate(B)[3] coating (185 F)	A.E.C. Lubricant	0.410	0.244	64.6	9	2	Some check marks
15	Ti-75A	Ditto	Molykote G	0.124	0.048	85.0	8	2	Ungalled
16	Ti-75A	Room-temperature fluoride-phosphate coating	Ditto	0.144	0.038	93.1	16	7	Smooth, ungalled
17	Ti-75A	Ditto	"	0.144	0.035	94.0	17	8	Ditto
18	Ti-75A	"	"	0.144	0.035	94.0	17	8	"
19	Ti-75A	Fluoride-phosphate coating and heat treatment	"	0.124	0.048	70.0	7	1	Ungalled, no check marks
20	Ti-75A	Fluoride-borate coating (185 F)	Lacquer-MoS_2	0.125	0.076	63.0	8	2	Rough, ungalled
21	Ti-75A Tube	Fluoride-phosphate coating (185 F)	Bonderlube 235	0.425 x 0.045	0.380 x 0.031	66.5	4	1	Galled

(1) This table represents a summary of the more significant drawing tests made. No annealing was done between passes.
(2) Fluoride-phosphate Coating A: pH-3.3.
(3) Fluoride-phosphate Coating B: pH-5.2.

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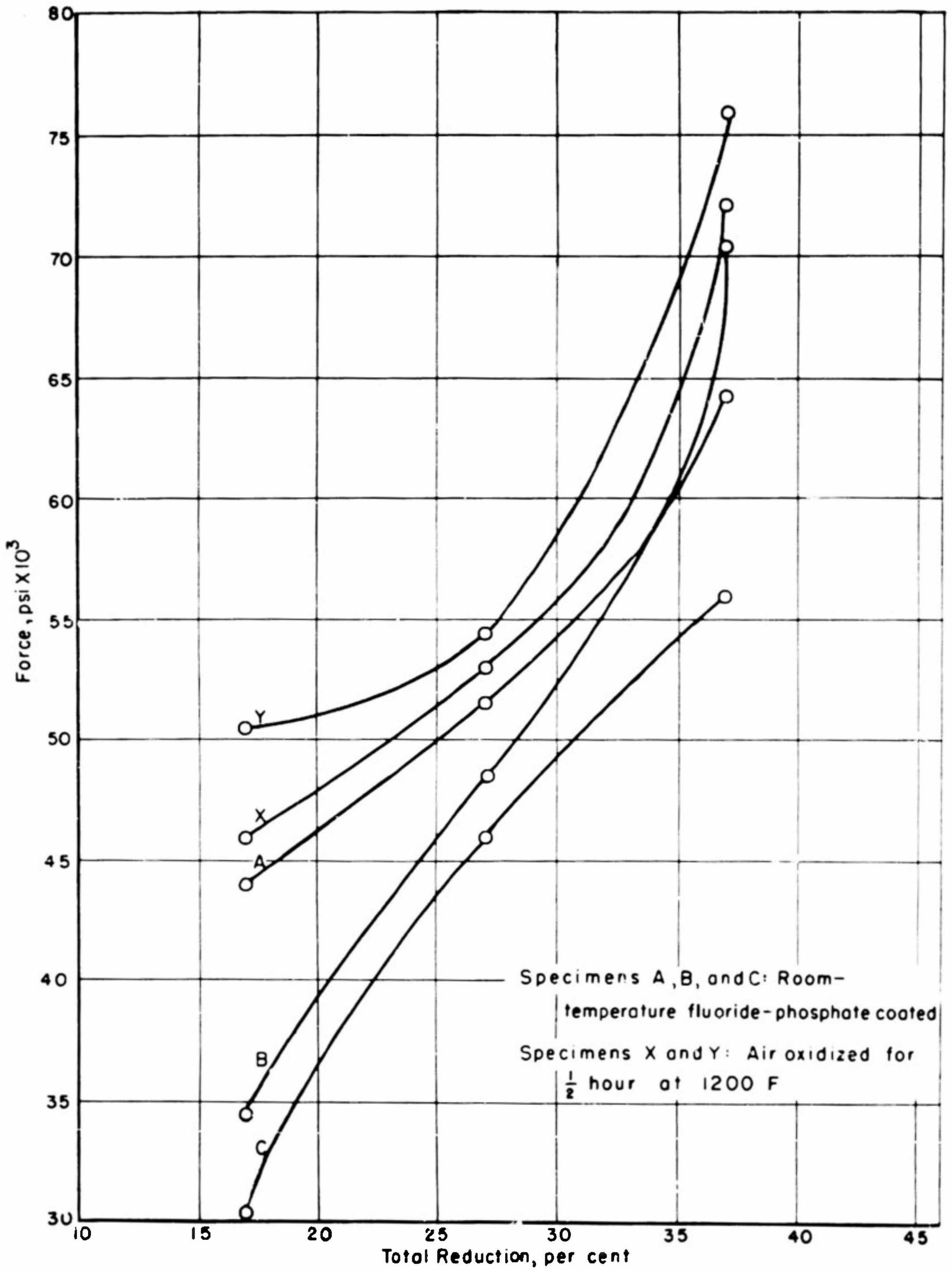

FIGURE 10. COMPARISON OF DRAWING FORCES REQUIRED FOR SIMPLE OXIDIZED AND IMMERSION-COATED Ti-75A USING MOLYKOTE G LUBRICANT

A-8130

Wire drawing with 22-foot lengths has been accomplished under simulated commercial conditions.

With the anodic coatings, as many as 7 passes (71.2 per cent reduction) were made without recoating or annealing. With the room-temperature fluoride-phosphate coating (Example 18, Table 4), 17 passes (94.0 per cent reduction) were made before it was necessary to anneal the wire. Recoating was necessary at intervals.

Tube drawing under commercial conditions was accomplished at Norristown, Pennsylvania, with the aid of the fluoride-phosphate immersion coating. Superior Tube Company drew the coated tubing in a very severe plug-drawing operation. The coating plus the drawing lubricant gave successive draws with a maximum of 66.5 per cent reduction (Example 21, Table 4).

The fluoride-phosphate immersion coatings possess several advantages over present methods of preparing titanium for drawing, such as metal sheathing or high-temperature oxidation. These are: (1) ease of application, no cumbersome plating process; (2) no exposure at high temperatures to form an oxide coating, which may cause embrittlement of the metal upon repeated drawing; (3) simple low-cost bath operation; and (4) ease of coating removal with no loss of expensive metal sheathing.

Reciprocating Wear

Coated titanium specimens were subjected to reciprocating wear tests under No. 30 oil against hardened steel with loads of 200 to 2500 psi. The machine (Figure 11) reciprocated 23 times per minute using a 4-1/4-inch stroke. When a coating failure occurred, the titanium metal seized to the steel wear plate and automatically shut off the machine.

The severity of this test lies in the change from hydrodynamic (uniform film) lubrication to boundary film (thin or discontinuous film) lubrication as the specimens reverse direction in their reciprocating motion. It is believed that this test gives a reasonable indication of the durability of the coatings for types of wear involving relatively slow motion and heavy loads.

Table 5 lists the more significant reciprocating wear-test results. It can be seen from the data that the wear of bare titanium against steel or titanium was very severe and galling took place immediately. Coated titanium showed only a slight improvement. Heating bare titanium in air at 800 F for 2 hours produced some increase in wear resistance. The most significant increase in wear resistance, however, was brought about by heating the immersion coatings in air for 3 to 5 hours at 800 F. Specimens thus treated were undamaged at the end of tests lasting for 780 hours or more (1 million strokes).

TABLE 5. RECIPROCATING WEAR TESTS OF TREATED TITANIUM

Example No.	Heat Treatment Time, hours	Heat Treatment Temperature, F	Type of Wear Surfaces (Specimen-Wear Plate)	Alloy	Load	Lubricants, Additives, Etc.	Total Number of Strokes	Total Running Hours	Final Condition of Specimens
1	--	--	Bare titanium - steel	130B	400	SAE No. 30 oil	2	--	Galled (immediately)
2	--	--	5% NaOH anodic coating - steel	75A	400	Ditto	17	--	Galled
3	--	--	Fluoride-phosphate coating - steel	75A	400	"	15	--	"
4	1	800	Heat-treated bare titanium - steel	75A	2500	"	4500	3.3	"
5	1	600	Heat-treated fluoride-phosphate coating - steel	75A	2500	"	2462	1.8	"
6	1	600	Ditto	75A	2500	"	2462	1.8	"
7	(10 min)	800	"	130B	400	"	2875	2.1	"
8	0.5	800	"	75A	1250	"	130,305	94.5	Polished, ungalled
9	0.5	800	"	75A	2500	"	18,335	13.3	Galled
10	1	800	"	75A	1250	"	385,220	279.0	Thin, ungalled
11	1	800	"	130B	1250	"	300,121	218.0	Polished, ungalled
12	2	800	"	130B	1250	"	544,006	394.0	Ditto
13	2	800	"	75A	2500	"	601,358	444.0	Galled
14	3	800	"	75A	2500	"	1,018,298	737.0	Smooth and undamaged
15	3	800	"	130B	2500	"	1,013,140	735.0	Ditto
16	5	800	"	75A	2500	"	1,156,898	837.0	"
17	3	800	"	130B	2500	SAE No. 30 oil, 0.1% silica contaminant	107,496	78.0	Galled
18	5	800	"	75A	2500	Ditto	193,527	140.0	Ditto
19	3	800	"	75A	2500	SAE No. 30 oil; 0.1% silica contaminant +0.1% MoS_2	252,100	183.0	"
20	0.5	800	Heat-treated fluoride-borate coating - steel	75A	2500	SAE No. 30 oil	18,368	13.3	Galled
21	1	800	Ditto	75A	2500	Ditto	79,581	57.6	Ditto
22	3	800	"	75A	2500	"	1,077,317	780.0	Smooth, polished, ungalled
23	5	800	"	130B	2500	"	1,013,140	735.0	Ditto
24	5	800	"	75A	2500	SAE No. 30 oil; 0.1% silica contaminant	143,258	104.0	Galled
25	--	--	Bare titanium - bare titanium	130B	600	SAE No. 30 oil	4	--	Galled
26	--	--	Fluoride-phosphate coating - fluoride-phosphate wear plate	75A	600	Ditto	17	--	Ditto
27	2	800	Heat-treated fluoride-phosphate coating - heat-treated fluoride-phosphate wear plate	130B	1250	"	142,090	103.0	"
28	--	--	Fluoride-phosphate coated; Moly-resin No. 105, 12-hour cure	75A	2500	Unlubricated	96,176	70.0	Polished, undamaged, no measurable wear

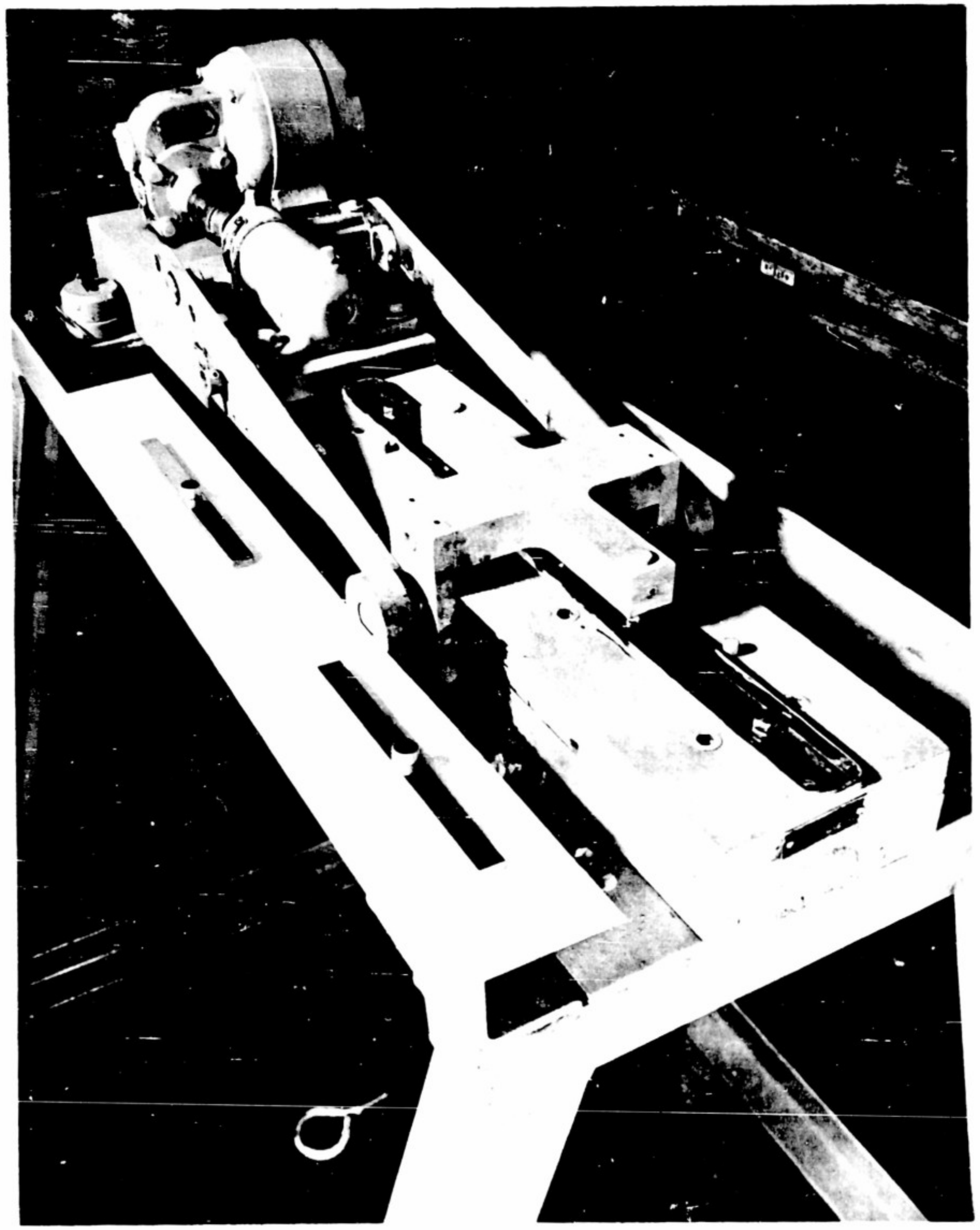

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FIGURE 11. RECIPROCATING WEAR-TEST MACHINE

Rotary Wear

Figure 12 shows the machine used for high-speed rotary wear tests. In the tests, two cylindrical button-type specimens were forced under pressure against a hardened steel disk which rotated at 910 feet per minute. The specimens also rotated at the same speed against the rotation of the large disk, resulting in extremely high sheering stresses at the points of contact. Coefficient-of-friction measurements were made between the specimens and the disk by a planatory gear dynamometer.

Because high-speed wear of metal surfaces presents a severe lubrication problem, an attempt was made to improve lubrication by maintaining a continuous film of molybdenum disulfide between the coated titanium surface and the steel wear plate. The MoS_2 was incorporated in an Epon phenolic resin, applied to a coated or a heat-treated surface, and cured as described previously.

Table 6 lists the results of the more significant high-speed rotary tests. The data show that the wear of bare titanium against steel was very severe: galling occurred almost immediately. The immersion coating alone did not appreciably improve the galling resistance. Coatings that were given an air heat treatment showed some improvement in wear resistance. The greatest improvement in wear resistance was made with a MoS_2-Epon resin layer bonded to the coated titanium metal. The wear-test results of this type of surface are comparable to and even better than those of carburized or nitrided titanium, and the specimens still retain their original core properties.

Paint Adhesion

Bare panels and some treated anodically were painted with an olive-drab paint (Military Specification TT-E-485B) and air dried. Tests made by scraping with a sharp knife blade showed much better adhesion for the treated panels.

An indirect adhesion test was also made by immersing painted samples in hot water (185 F) for one week. Some blistering occurred on all panels, but much less blistering was evident on the panels which had been anodized. Figure 13 shows results for such tests on RC-55 and Ti-75A panels.

CONCLUSIONS

Several interesting and useful conversion coatings have been developed for titanium. Of particular interest is the immersion coating that can be produced at room temperature. The present investigation has carried the

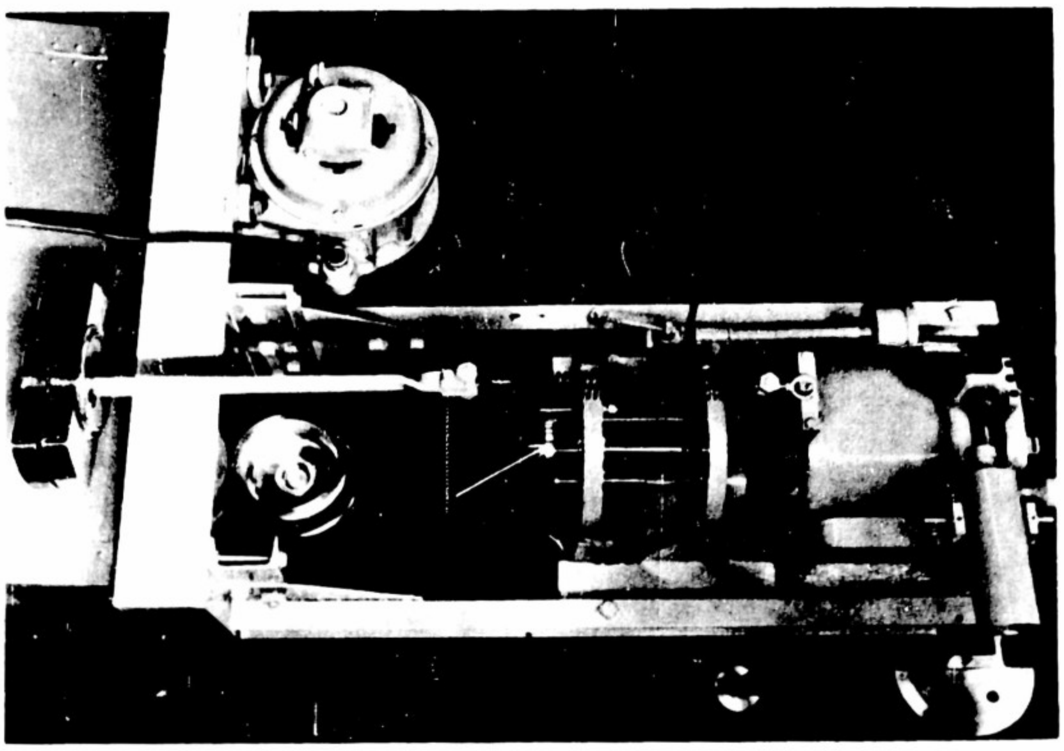


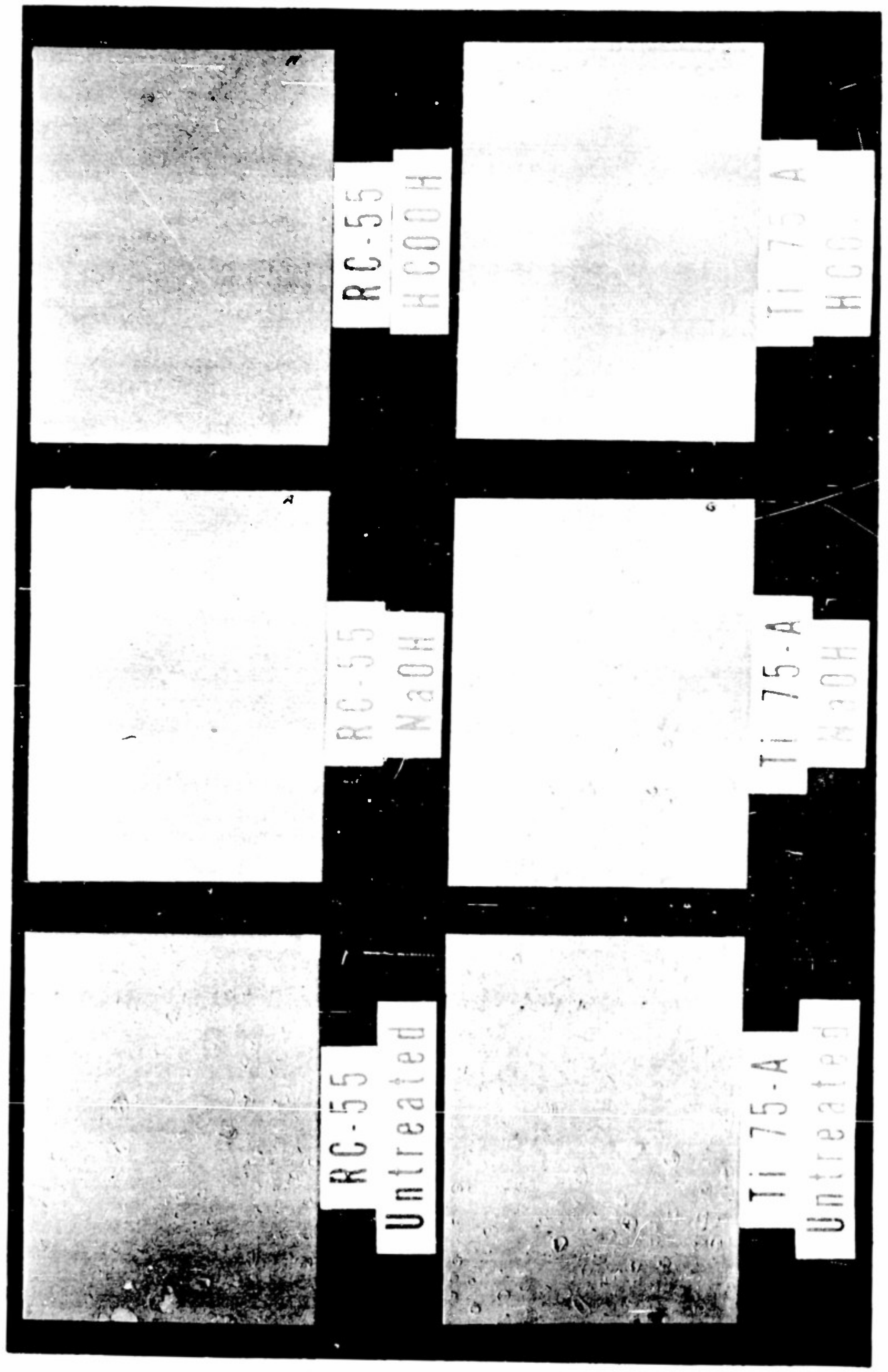
FIGURE 12. HIGH-SPEED ROTARY WEAR MACHINE

Arrow points to large steel wear plate

TABLE 6. ROTARY WEAR TESTS OF TREATED TITANIUM(1)

Example No.	Specimen Treatment or Condition	MoS_2-Resin Ratio	Resin Curing Time, hours	Load, psi	Total Time Run, hours	Average Coefficient of Friction	Final Condition of Specimens
1	No coating	--	--	--	0	--	Galled, seizure occurred instantly
2	Ditto	--	--	--	0	--	Ditto
3	5% NaOH anodic coating	--	--	300	(15 sec)	--	Severely galled
4	Ditto	--	--	300	(15 sec)	--	Ditto
5	Fluoride-oxalate coating	--	--	300	(30 sec)	--	"
6	Ditto	--	--	300	(60 sec)	--	"
7	Fluoride-phosphate coating	--	--	400	(30 sec)	--	Galled
8	Heat-treated fluoride-phosphate coating (heat treated 5 hours)	--	--	400	3.6	0.047	"
9	Heat-treated fluoride-phosphate coating (heat treated 19.5 hours)	--	--	600	6.7	0.014	"
10	Bare titanium, Moly-resin layer(2)	1:1.5	8	600	(40 min)	--	"
11	Heat-treated, bare titanium; Moly-resin layer(2)	1:1.5	8	600	(44 min)	--	"
12	Heat-treated, fluoride-phosphate coating, Moly-resin layer(2)	1:1.5	2	600	0.5	--	"
13	Ditto	1:1.5	8	600	36.5	--	"
14	"	1:1.5	10	600-800	199.0	0.017	Undamaged at termination of test
15	"	1:2	8	600	71.0	0.057	Galled
16	"	1:2	10	600	161.5	0.062	Specimens did not gall, but friction increased greatly
17	"	1:2	12	600-800	225.0	0.072	Undamaged at termination of test
18	Fluoride-phosphate coating; Moly-resin layer(2)	1:2	12	800	273.5	0.069	Ditto

(1) All tests were run under SAE No. 30 oil.
(2) MoS_2 in an Epon phenolic resin.



Panel 91079

FIGURE 13. PAINT DURABILITY ON TITANIUM PANELS

Olive drab paint; Military Specification TT-E-485-B; hot-water immersion, 1 week, 185 F

work to the point where it has been possible to demonstrate the utility of such treatments. However, it is realized that the processes are not yet at the stage for commercial use on a large scale. The next step is, therefore, a shift from the laboratory to the pilot-plant scale. Such a program would undoubtedly result in a commercial process for treating titanium.

Data contained in this report and in all the Interim Technical Reports are recorded in BMI Laboratory Notebooks Nos. 6320, 6593, 7182, and 7799.

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